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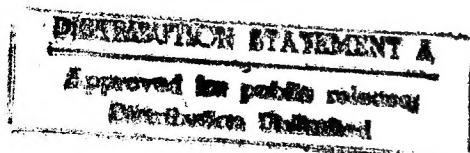*U.S. Army Research Laboratory*
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THE EFFECT OF POLYMER CHAR ON NITRIDATION KINETICS OF SILICON

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SUMMARY

Effects of polymer char on nitridation kinetics of attrition milled silicon powder have been investigated from 1200 to 1350 °C. Results indicate that at and above 1250 °C, the silicon compacts containing 3.5 wt% polymer char were fully converted to Si_3N_4 after 24 hr exposure in nitrogen. In contrast, the silicon compacts without polymer char could not be fully converted to Si_3N_4 at 1350 °C under similar exposure conditions. At 1250 and 1350 °C, the silicon compacts with polymer char showed faster nitridation kinetics than those without the polymer char. As the polymer char content is increased, the amount of SiC in the nitrided material is also increased. By adding small amounts (~2.5 wt%) of NiO, the silicon compacts containing polymer char can be completely nitrided at 1200 °C. The probable mechanism for the accelerated nitridation of silicon containing polymer char is discussed.

INTRODUCTION

Polymeric materials are being used quite extensively in the processing of ceramics for a variety of reasons: for improving dispersion of ceramic powders in a solvent (refs. 1 and 2), for improving flow characteristics and consolidation behavior of ceramic powders (refs. 3 to 5), for forming ceramic bodies into complex shapes (refs. 6 to 9), for coating ceramic powder onto ceramic fiber, as precursor material for ceramic matrix or ceramic fiber (refs. 10 to 12), and as a source of carbon (refs. 13 and 14). When used as a binder for ceramic powders, the polymeric material is chosen based on its forming characteristics and its influence on the densification and sintering behavior of the ceramics.

In general, polymeric materials when pyrolyzed leave a char of carbon whose amount can be varied from ~0 to 65 percent depending on the physical and chemical characteristics of the polymer. The acrylic binders generally used for the fabrication of SiC and Si_3N_4 ceramics leave less than 1 wt% polymer char on pyrolysis (refs. 6 to 9) and are known not to interfere with the sintering kinetics of these ceramics. For the fabrication of reaction-formed silicon carbide, a high char-yield polymer is deliberately chosen as a source of carbon. When this polymer is mixed with silicon in proper proportion and pyrolyzed below 1000 °C, it typically yields a mixture of silicon and carbon which upon heating to 1450 °C results in a SiC matrix with minimum amounts of free silicon or carbon (ref. 15). The situation is quite different in the fabrication of reaction-bonded silicon

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nitride using polymeric materials. Although, the effect of polymer char on the nitridation kinetics of commercially available silicon powders (average particle size >3 μm) has not been investigated, a recent study (ref. 16) has shown that the polymer char of some polymers typically used for ceramic processing affects the nitridation kinetics of laser synthesized, high purity sub-micron silicon powder in nitrogen between 1250 °C and 1350 °C. Chars of polymers such as, polyethylene and polystyrene do not affect the nitridation kinetics and complete conversion of silicon to silicon nitride is achieved within an hour of exposure. However, chars of polymers such as halogenated ethylene, polymethylmethacrylate, and polysilazane retard the nitridation kinetics of the same powder at both temperatures, and complete conversion of silicon to silicon nitride is not achieved even after 30 hr exposure.

Sub-micron silicon powders, fugitive polymeric binders, and nonaqueous solvents are also being used for the fabrication of SiC fiber-reinforced RBSN composites (ref. 17). Such composites are under development and evaluation for aircraft gas turbine applications. The reinforcement for the RBSN composites can be either monofilaments or fiber tows. To facilitate infiltration of silicon powder between monofilaments or filaments in the fiber tows or in two-dimensional woven fiber mats, sub-micron silicon powders are used. The polymer binders used for the fabrication of SiC monofilament-reinforced RBSN composites leaves less than 1 percent polymer char in the green bodies (ref. 17). This amount of polymer char does not interfere with the nitridation process of the composites. However, the same polymer binder system can not be used for the fabrication of small diameter(<20 μm) SiC fiber reinforced RBSN composites because of its poor forming characteristics. Therefore, an entirely different polymer binder system must be used. One possible candidate is the polyvinyl-based system.

The objectives of this study are two-fold. First, to investigate the effects of residual char of polyvinyl and polyvinylidene polymers on the nitridation kinetics of sub-micron silicon powder. Second, to determine the nitridation mechanism of silicon in the presence of the polymer char alone and in combination with the nitridation enhancing additive, NiO.

EXPERIMENTAL

A commercial grade silicon powder (Union Carbide, NY), thermoplastic polymer binders and additives, and NiO powder (Baker Chemicals) were chosen as the starting materials. The average particle size of the as-received silicon powder was ~6μm. A vinyl-based polymer was used as the polymer additive. The choice of the polymer binder and additive and their weight fractions depended on the forming characteristics of the total system and the char yield of the polymers upon pyrolysis in nitrogen. As individual components, typical polymer char yields for the chosen polymer binder and additive were 5 and 33 percent, respectively.

To reduce particle size, the as-received silicon powder was attrition milled for 36 hr in a 2-liter sintered reaction-bonded silicon nitride vessel (Allied Signal Ceramics Company, Torrance, CA) filled with hot-pressed silicon nitride balls (HPSN) and tetrahydrofuran (THF) solvent. The media charge was 300 gm of silicon powder, 2400 gm of 6 mm diameter HPSN balls, and 1 liter of THF. Some batches contained as-received silicon alone, and others contained as-received silicon with 2.5 wt% NiO. After attrition milling, the silicon-solvent slurry was stored in a sealed polyethylene bottle until further use.

For ease of specimen preparation, tape casting was chosen as a method of fabrication. The same method is also being used for the preparation of preforms of SiC/RBSN composites. For tape casting, the polymer binder and additive mixture were first dissolved in a THF solvent, and then silicon and THF slurry were added to the polymer solution. For all batches, the weight ratio of silicon to the total polymer content was maintained at 80:20. Although the total polymer content was kept constant, the polymer additive to binder content was varied from 0 to 50 wt% to achieve desirable amounts of polymer char in the silicon tapes. The resultant slurry was

ultrasonically stirred and cast on a Teflon plate to form a tape. The tape was dried for several hours in air to remove excess solvent. Typical thickness of the dried tape was ~2 to 3 mm.

For the nitridation experiments, disc specimens, each with dimensions of 15 mm in diameter and 2 to 3 mm in thickness, were cut from the tapes. Each specimen was first pyrolyzed between 200 and 550 °C and then nitrided at 1200, 1250, and 1350 °C in a high temperature furnace equipped with a thermogravimetric recording micro-balance (Perkins Elmer, TGA 7 Series). High purity nitrogen (99.999 percent) was flowed through the TGA at a rate of 60 cc/min.

The nitrided specimens were ground to powder and analyzed by x-ray diffraction. Determination of the amounts of typical phases such as, β-SiC, α- and β-Si_3N_4, and unreacted Si was accomplished by using a technique reported in the literature (ref. 18). The total oxygen and carbon contents in the specimens were determined by chemical analysis.

RESULTS

The impurity content, average particle size, and surface area of the silicon powder before and after attrition milling are shown in Tables I and II, respectively. Data show that after attrition milling, the average particle size of the as-received silicon decreased from 6 μm to 0.64 μm and the average surface area increased by an order of magnitude from 1.6 to 30.2 m^2/gm. As expected, the oxygen content of the attrition milled powder increased significantly due its smaller particle size and greater surface area. The attrition milling also introduced extraneous impurities such as, yttrium and aluminum from the milling media into the silicon powder.

Typical isothermal nitridation curves of attrition milled silicon powder compacts with and without 3.5 wt% polymer char between 1200 and 1350 °C in nitrogen are shown in figure 1. The curves show three distinct weight gain regions; a very rapid initial weight gain region followed by a slow weight gain region and then a plateau region where weight remained nearly constant. Comparison of the curves at 1200 and 1250 °C indicates that at any exposure time, the silicon compacts containing polymer char showed significantly higher weight gain than the silicon compacts without polymer char. The higher weight gain reflects higher conversion of silicon to silicon nitride. At 1250 and 1350 °C, the reaction rates were faster in the first and second regions of nitridation for the silicon compacts with polymer char compared to those of silicon compacts without polymer char. In addition, the TGA curve of the silicon compact with polymer char leveled off after one hour of exposure. The silicon compacts without polymer char nitrided at 1350 °C gained ~52 wt% after ~9 hr exposure. This is ~10 wt% higher than the weight gain observed for the silicon compacts with polymer char. Theoretically ~66 percent weight gain is expected when silicon completely converts to silicon nitride. However due to loss of silicon monoxide gas which is formed due to oxidation of silicon (a reaction between residual oxygen present in flowing nitrogen and silicon) and active oxidation of silica on silicon powder, complete conversion of the initial silicon to silicon nitride may not be possible. As a result, the weight gain seen is normally lower than the theoretical value.

The influence of the nitridation enhancing additive, NiO, on the nitridation kinetics of polymer char containing silicon compacts was also studied. Typical isothermal TGA curves for the silicon compacts with polymer char, and with and without 2.5 wt% NiO at 1200 °C in 1 atm nitrogen are shown in figure 2. Addition of a small amount of NiO to the silicon compacts containing polymer char permitted full conversion of silicon to silicon nitride at 1200 °C within 24 hr. The fact that the silicon compact with NiO can be nitrided at a lower temperature than the silicon compacts with polymer char alone suggests that the mechanism of nitridation in these two systems can be different.

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A summary of XRD data for the nitrided TGA specimens are shown in Table III. The table shows that the silicon compacts with polymer char nitrided at 1350 °C for 3 hr, and those with polymer char and NiO nitrided at 1200 °C for 24 hr contained less than 1 percent residual silicon and small amounts of SiC; an indication of near complete conversion of silicon to either Si_3N_4 or SiC. The silicon compacts with polymer char alone nitrided at 1250 °C for 24 hr achieved a high degree of conversion, but those nitrided at 1200 °C did not nitride completely even after 48 hr exposure.

To determine if carbothermic reaction might be responsible for the accelerated nitridation in silicon compacts containing polymer char, nitridation experiments were performed on fumed silica (CAB-O-SIL fumed silica L-90) and carbon black (Monarch 1300) at 1200 and 1350 °C in 1 atm nitrogen in a TGA. Three different molar ratios of carbon to silica (C/SiO_2) were used; 3:1, 5:1, and 15:1. A C/SiO_2 ratio of 3 corresponds to that present in the silicon compacts containing polymer char. The particle size and surface area of fumed silica and carbon black are given in Table IV. The TGA results (shown in fig. 3) indicate that at 1200 °C (fig. 3(a)) and 1350 °C (fig. 3(b)), the compacts of carbon and fumed silica lost between 8 to 11 percent and ~20 to 27 percent of their initial weight, respectively, depending upon their molar ratios after 12 hr exposure. Furthermore, the weight loss for these compacts seems to increase with increasing molar ratio and temperature, but the temperature had a greater influence on the weight loss than did the molar ratio.

XRD analysis showed no evidence of crystalline phase in the compacts at all three molar ratios of carbon to silica nitrided at 1200 °C. Those nitrided at 1250 and 1350 °C, irrespective of the molar ratios, showed α-Si_3N_4. Chemical analysis of these compacts identified unreacted carbon and small amounts of silica in the compacts nitrided at temperatures lower than 1350 °C indicating partial reaction between the silica and carbon. The formation of α-Si_3N_4 suggests carbothermic reaction between silica and carbon black.

These results support a mechanism in which the silica layer on silicon powder reacts with polymer char to initiate carbothermal reaction provided the surfaces of the silicon and polymer char are highly active.

To determine the effect of polymer char amount on the phase composition of the nitrided material, the silicon compacts containing varying amounts of polymer char were nitrided in a graphite furnace at 1200 °C for 24 hr, and at 1350 °C for 1 hr. After nitridation, the compacts were analyzed for crystalline and non-crystalline phases by XRD and chemical analysis, respectively. XRD phase analysis of the silicon compacts with polymer char, and with and without NiO at 1200 ° for 24 hr are shown in figure 4. It is clear from figure 4(a) that as the polymer char content is increased in the silicon compacts without NiO, the amounts of SiC and total Si_3N_4 increased, and the amount of unreacted silicon decreased. The α/β ratio which is an indicator of Si_3N_4 formation by gas phase reactions also decreased with increasing polymer content. Theoretically, if carbon were to react only with the silicon, we expect 3.33 grams of SiC for each gram of carbon. The fact that the wt% of SiC formed was nearly three times the wt% of polymer char indicates that most of the polymer char is reacting with the silicon. On the other hand, the silicon compacts containing NiO nitride under similar conditions (fig. 4(b)) showed no significant effect of polymer char content on the amounts of Si_3N_4 and SiC. Comparison of figures 4(a) and 4(b) indicates that the amount of SiC formed in the nitrided silicon compacts with polymer char and NiO is lower than those with polymer char alone.

Figures 5(a) and (b) show the XRD phase analysis of silicon compacts with and without NiO, and with varying amounts of polymer char nitrided at 1350 °C for 1 hr. In the absence of NiO, with increase in polymer char content the amount of SiC also increased, but the amount of the unreacted silicon initially decreased and then leveled off, and the amount of total Si_3N_4 formed initially increased and then leveled off. The α/β ratio also decreased with increasing polymer char content. On the other hand, the silicon compacts with NiO under similar nitriding conditions showed decreasing amounts of total Si_3N_4 and increasing amounts of SiC with increasing amount of polymer char. The amount of unreacted silicon was below the detectable limit. Again the

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amounts of SiC formed in the silicon compact with NiO were consistently lower than those in the compacts without NiO.

The carbon elemental analysis results showed that the silicon compacts blended with NiO and nitrided at 1250 and 1350 °C had up to 1.1 wt% excess carbon depending on the polymer char content in the pre-nitrided compacts. The presence of excess carbon indicates that the polymer char did not completely react with silicon, and thus helps in explaining the lower SiC content in these compacts.

The quantitative analysis of the silicon compacts, those containing both NiO and polymer char, and those containing polymer char alone, nitrided at 1200 and 1350 °C indicated a total oxygen content of ~3 percent. This is nearly half that of the attrition milled silicon powder (cf. Table II). Assuming that all of the oxygen in the nitrided compacts is associated with silicon nitride as SiO_2 and with NiO, the calculated total silica content in the nitrided compacts is ~6 percent. The fact that silica content remained nearly the same in the nitrided compacts with and without polymer char suggests that polymer char has no influence on the total silica content of the nitrided compacts.

DISCUSSION

Results of this study indicate beneficial effect of polymer char on the nitridation kinetics of attrition milled silicon at and above 1250 °C. The mechanism by which polymer char enhances nitridation can be analyzed based on its reactivity with silica on silicon powder and its ability to lower the partial pressure of oxygen in the system which incidentally also influences formation of α-Si_3N_4.

In general, silicon powder—as-received or attrition milled—contains a small layer of silica whose thickness can vary from ~ 3 to 4 nm. Unless this silica layer is disrupted either physically or chemically, the nitridation reaction does not start (ref. 19). After the initiation, the extent to which nitridation reaction proceeds is controlled by several factors: mean particle size and size distribution; the nature and distribution of impurities in the starting silicon powder; size and size distribution of open porosity in the silicon compacts; dimensions of the silicon compacts; and nitriding conditions. To remove the silica layer on the silicon powder two techniques have been successfully used; annealing the silicon compacts in H_2 (ref. 20) or a mixture of N_2+H_2, (ref. 21) or adding a small amount of a transition metal oxide, such as Fe_2O_3, NiO, MnO, Cr_2O_3 to the silicon compacts (ref. 19).

In the first approach, the silicon compacts are annealed in a stream of flowing hydrogen or hydrogen containing gases between 1000 and 1200 °C for 1 to 2 hr. At these temperatures hydrogen reacts with silica, and the by-products of the reaction, SiO gas and water vapor, are removed by the flowing gas. Studies (refs. 20 and 21) have shown that the hydrogen annealed silicon compacts when nitrided at 1350 °C, consistently showed faster nitridation kinetics than those of the unannealed silicon compacts, but similar compacts when oxidized before nitridation showed slower nitridation kinetics.

In the second approach, a nitridation enhancing additive is used to disrupt the silica on silicon. Although the mechanism by which the additive operates is not clearly understood, it is generally believed that silica on the silicon reacts with the additive to form a porous silicate layer and this exposes the fresh surface of silicon for nitridation (ref. 19).

It is well established in RBSN literature that during nitridation, Si_3N_4 is formed by the reaction of silicon and SiO vapors with nitrogen or by the direct reaction of solid silicon with nitrogen (ref. 19). The silicon nitride phase formed by the gas phase reactions, i.e., by silicon vapors with nitrogen or by SiO vapors with nitrogen is predominantly α-Si_3N_4 (ref. 22), and that formed by the solid silicon with nitrogen (ref. 19 and 23) or by the

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dissolution α-Si_3N_4 and reprecipitation from the silicate melt is β-Si_3N_4 (refs. 19 and 24). Thus from the knowledge of α/β ratio, it is possible to determine which of these two reactions will be dominant during nitridation.

The fact that the silicon compacts containing polymer char showed faster nitridation kinetics at 1250 °C or greater, similar to those reported in the literature for the silicon compacts pre-treated in hydrogen, suggests that polymer char reacts with the native silica on the surface of silicon powder similar to the hydrogen reaction with silica.

In the SiO_2-C-N_2 system (refs. 25 and 26), it is known that SiC, Si_3N_4, SiO and Si_2ON_2, form between 1200 and 1600 °C. The suggested overall reactions for the formation of these products are as follows;

$$SiO_2 + 3C = SiC + 2CO \tag{1}$$

$$SiO_2 + C = SiO + CO \tag{2}$$

$$2SiO_2 + N_2 + 3C = Si_2N_2O + 3CO \tag{3}$$

$$3SiO + 2N_2 = Si_3N_4 + (3/2)O_2 \tag{4}$$

The conditions under which SiC, Si_2N_2O, and Si_3N_4 phases are stable depend upon the mole ratio of carbon to silica, partial pressures of oxygen and nitrogen, and reaction temperature. Previous studies have shown that the formation of SiC is favored when the mole ratio of carbon to silica is greater than 3 and at temperatures greater than 1400 °C (ref. 27), and that the formation of Si_3N_4 is favored at mole ratios of carbon to silica less than 3 and at temperatures less than 1650 °C (ref. 28). It is also known that the formation of silicon oxynitride can be avoided in the presence of excess carbon because carbon maintains the partial pressure of oxygen much lower than 10 to 20 atm (ref. 23). Since silicon oxynitride phase was not detected by XRD analysis and since the carbon to silica mole ratio used in the current study was lower than 3, the formation of silicon carbide by equation (1) and the formation of oxynitride by equation (3) can be ruled out. From the process of elimination, we conclude that equation (2) is the dominant reaction under the current experimental conditions. The by-products of this reaction are SiO and CO. The SiO, being a reactive gas and an intermediary, can further react with nitrogen to form α-Si_3N_4. The other reaction product, CO, can partially react with silica or silicon or be swept away with the flowing nitrogen.

After the silica layer on silicon is removed by the carbothermic reaction, the pristine surface of silicon can react with excess polymer char or nitrogen, and the excess polymer char can also react with residual oxygen present in the system as shown below:

$$3Si + 2N_2 = Si_3N_4 \tag{5}$$

$$Si + C = SiC \tag{6}$$

$$2C + O_2 = 2CO \tag{7}$$

Combining equations (2), (4) to (6), and (7) yields

$$4Si + 3SiO_2 + 7C + 4N_2 = 2Si_3N_4 + SiC + 6CO \tag{8}$$

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The free energy of formation, ΔG, for Reaction 8 at 1200 °C is −74.4 K cal/mole. Even though this reaction is thermodynamically feasible at this temperature, complete conversion of silicon to Si_3N_4 may not be possible due to kinetic reasons as seen in figure 3(a). The phase analysis results of the nitride silica/carbon compacts, and the silicon compacts containing polymer char clearly show that to obtain significant amount of Si_3N_4, a nitridation temperature greater than 1200 °C is required.

Although carbothermic reaction is probably responsible for faster nitridation kinetics in the silicon compacts containing polymer char, it is not clear whether the polymer char locally disrupts or completely removes the silica layer on silicon. As reported earlier, the attrition milled silicon powder contains ~6 wt% oxygen. Assuming that all the oxygen is in the form of silica, the total calculated amount of silica in the silicon compact is ~12 wt%. To completely remove this amount of silica requires at least 3 wt% of carbon char. Therefore, as the polymer char content in the silicon compacts is increased up to 3 wt%, we should expect increasing amounts of SiO and CO according to equation 2. Increasing amounts of SiO implies greater amounts of α-Si_3N_4 and increasing α/β ratio in the nitrided compacts. However, figures 4(a) and 5(a) show that at low concentrations of polymer char (~1.5 percent), the nitride silicon compacts show α/β ratios of 2.5 to 3 and at high concentrations (>2.5 percent), the α/β decreases to less than 1. This also implies that at higher concentration of polymer char, SiO and hence α-Si_3N_4 formation is retarded. A decrease in the partial pressure of SiO with increase in the polymer char content is possible if polymer char apart from reacting with the silica on silicon also reacts with residual oxygen generated as the by-product of the Reaction 4 or the oxygen possibly present in the flowing nitrogen. If these reactions were occurring, we should also expect lower amounts of silica in the nitrided compacts containing polymer char than those containing no polymer char. Contrary to the expectations, the silica content in the nitrided compacts remained nearly the same regardless of polymer char contents. This tends to suggest that polymer char possibly triggers nitridation reaction by locally reacting with the silica on the surface of silicon, but it does not completely remove the silica. The fact that most of the polymer char in the silicon compacts converts to SiC also supports a mechanism in which polymer char locally reacting with silica on silicon.

Whether the faster nitridation kinetics seen in the silicon compacts containing polymer char is primarily due to carbothermic reaction or due to synergistic effects of carbothermic reaction and impurities present in the silicon powder is not known. To prove the role played by polymer char in the nitridation reaction, further study is needed on high purity sub-micron silicon powder with polymer char.

Results also show that the addition of small amounts of nitridation enhancing additive, NiO, to polymer char containing silicon compacts does lower the nitridation temperature to 1200 °C, and complete conversion of silicon to silicon nitride is possible within reasonable exposure time (<24 hr). This suggests that NiO is much more effective in disrupting the silica scale on silicon and promoting nitridation than polymer char alone at lower temperatures. It is hypothesized that NiO, similar to Fe_2O_3 and other transition metal oxide, devitrifies silica or reacts with it to form a low melting nickel silicate. Both of these mechanisms facilitates direct access of nitrogen to silicon.

SUMMARY OF RESULTS

The effects of polymer char on the nitridation of silicon has been determined. The major findings are as follows:

(1) The silicon compacts containing polymer char showed faster nitridation kinetics than the silicon compacts without polymer char, and complete conversion to silicon nitride within 6 hr at and above 1250 °C. Removal of the silica layer on silicon powder by the polymer char appears to be the mechanism.

(2) As the amount of polymer char in the silicon compacts is increased, the amount of SiC in the nitrided compacts is also increased. It is suggested that the polymer char reacts with silica and then with silicon.

(3) The nitridation temperature of the silicon compacts with polymer char can be reduced to 1200 °C by adding small amounts (2.5 wt%) of nitridation enhancing additive, NiO.

CONCLUSION

The char of vinyl based polymer shows two beneficial effects on the nitridation kinetics of attrition milled silicon powder: (a) it disrupts silica on silicon and thus enhancing kinetics of nitridation, and (b) it acts as a scavenger for residual oxygen in the system. The polymer char and NiO containing silicon compacts can be completely nitrided at 1200 °C. The NiO additive is more effective agent for facilitating nitridation by disrupting the silica layer on the silicon powder than is the polymer char alone.

REFERENCES

1. Kerkar, A.V. and Feke, D.L.: Induced Flocculation in Sterically Stabilized Ceramic Powder Dispersions, Coll. and Surface., 53, p 363, 1991.

2. Kerkar, A.V., Henderson, R.J.M., and Feke, D.L.: Steric Stabilization of Ceramic Slip: I. Control of Particle Agglomeration and Packing, J. Am. Ceram. Soc. (Submitted for publication.)

3. Pincus, A.G. and Shipley, T.E.: The Role of Organic Binders in Ceramic Processing, Ceram. Ind. Magazine, 92 (4), p 106, 1969.

4. Rasmussen, E.H.: Instrumentation for Spray Drier, Am. Ceram. Soc. Bull., 39, pp. 732-734, 1930.

5. Richards, V.L.: Adsorption of Dispersants on Zirconia Powder in Tape-Casting Slip Compositions, J. Am. Ceram. Soc., 72 (2), pp. 325-327, 1989.

6. Edirisinghe, M.J. and Evans, J.R.G.: Review: Fabrication of Engineering Ceramics by Injection Moulding I, Materials Section, Int. J. High Technol. Ceram., 2 , pp. 1-31, 1986.

7. Carlsson, R.: The Shaping of Engineering Ceramics, Mater. Des.,10, pp. 10-14, 1989.

8. Mutsuddy, B.C.: Study of Ceramic Injection Molding Parameters, Am. Ceram. Soc. Bull., 68, pp. 1796-802, 1989.

9. Whalen, T.J. and Johnson, C.F.: Injection Molding of Ceramics, Am. Ceram. Soc. Bull., 60, pp. 216-20, 1981.

10. Yajima, S., Okamura, K., Hayashi, J., and Omori,M.: Synthesis of Continuous SiC Fibers with High Tensile Strength, J. Mater. Sci., 17, pp. 2371-83, 1982.

11. Rogers, J.J., Semen, J., and Yu. F., Daniel, Y.: Silicon Carbide and Silicon Nitride Structural Ceramics Derived from a preceramic Polymer Binder, Ceram. Eng. Sci. Proc., 10 [7-8] pp. 833-836, 1989.

12. Schwab, S.T. and Blanchard-Ardid, C.R.: The Use of Organometallic Precursors to Silicon Nitride, Mater. Res. Soc. Slump. Proc., 121, pp. 581-87, 1988.

13. Popper, P.: The Preparation of Dense Self-Bonded SiC, p 209 in Special Ceramics, Heywood, London, 1960.

14. Hucke, E.E.: Composite Bodies Comprising a Continuous Framework and Impregnated Metallic Material and Methods of Their Production, U.S. Pat. No.3235346, Feb., 1966.

15. Ness, J.N. and Page, T.F.: Microstructural Evolution of Reaction-Bonded Silicon Carbide," J. Mater. Sci., 21[4] pp. 1377-97, 1986.

16. Lightfoot, A., Parikh, R.S., Haggerty, J.S., and Sheldon, B.W.: Nitridation of Binder and Solvent Exposed High Purity Silicon Powder, Submitted to J. Am. Ceram. Soc.

17. Bhatt, R.T.: Effects of Fabrication Conditions on the Properties of SiC Fiber-Reinforced Reaction-Bonded Silicon Nitride Matrix Composites (SiC/RBSN), NASA TM–88814, 1986.

18. Mencik, Z. and Short, M.A.: Quantitative Phase Analysis of Synthetic Silicon Nitride by X-Ray Diffraction: An Improved Procedure, Ford Motor Co. TM–SR-72-98, 1972.

19. Moulson, A.J.: Reaction-bonded Silicon Nitride: Its Formation and Properties, J. Mater. Sci., 14, p 1017, 1979.

20. Rahaman, M.N. and Moulson, A.J.: The Removal of Surface Silica and Its Effect on the Nitridation of High-Purity Silicon, J. Mater. Sci., 19, pp. 189-194, 1984.

21. Lindey, M.W., Elias, D.P., Jones, B.F., and Pitman, K.C.: The Influence of Hydrogen in the Nitriding Gas on Strength, Structure and Composition of Reaction-Bonded Silicon Nitride," J. Mater. Sci., 14, [1] pp. 70-85, 1979.

22. Nihara, K. and Hirai, T.: Chemical Vapour Deposited Silicon Nitride-Part 3. Structural features. J. Mater. Sci., 12, 1233 (1977).

23. Blegen, K.: Equilibria and Kinetics in the System Si-N and Si-N-O, Special Ceramics, 6, Brit. Ceram. R.A., Stoke-on-Trent, pp. 223-244, 1975.

24. Naruse, W., Nojori, M., and Tada, M.: J. Jap. Inst. Metals, 35, p 731, 1971.

25. Komeya, K. and Inoue, H.: Synthesis of α Form of Silicon Nitride from Silica, J. Mat. Sci., 10, pp. 1243-1246, 1975.

26. Lee, J.G. and Cutler, I.B.: Formation of Silicon Carbide From Rice Hulls, Ceram. Bull., 54 (2), pp. 195-198, 1975.

27. Lee, J.G. and Cutler, I.B.: Reactions in SiO_2-C-N_2 System" Nitrogen Ceramics, ed. F.L. Riley, Noordhoff, Leyden, 187, 1977.

28. Hendry, A. and Jack, K.H.: The Preparation of Silicon Nitride From Silica, Special Ceramics, 6, Brit. Ceram. R.A., Stoke-on-Trent, pp. 199-208, 1975.

TABLE I.—TRACE IMPURITY ANALYSIS OF
SILICON POWDER BEFORE AND AFTER
ATTRITION MILLING

Elements	As-received silicon, wt%	36 hr attrition milled silicon, wt%
Aluminum	0.17±0.017	0.20±0.002
Iron	0.50±0.050	0.40±0.004
Calcium	0.01±0.001	0.01±0.001
Chromium	0.03±0.003	0.02±0.002
Manganese	0.04±0.004	0.05±0.005
Titanium	0.01±0.001	0.01±0.001
Vanadium	0.01±0.001	0.01±0.001
Ziroconium	0.02±0.002	0.01±0.001
Yttrium	0.01±0.001	0.20±0.002

TABLE II.—CHEMICAL ANALYSIS, SURFACE AREA, AND
AVERAGE PRTICLE SIZE OF SILICON POWDER

Material	Oxygen, wt%	Carbon, wt%	Surface area, m^2/g	Average particle size, μm
As-received	0.43±0.04	0.025±0.001	1.6±0	6.0
Attrition milled for 36 hr	6.0±0.06	0.30±0.003	30.2±3	0.64

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TABLE III.—PHASE COMPOSTION RESULTS OF NITRIDED TGA SPECIMENS

System	Polymer char prior to nitridation, wt%	Nitriding temperature, °C	Crystalline after phase nitridation distribution			Nitridation time, hr
			Si_3N_4, wt%	SiC, wt%	Si, wt%	
Si	0	1200	36.2	0	63.8	64
Si + ploymer binder + polymer additive	3.5	1200	72.4	7.8	19.8	48
Si + polymer binder + 2.5 wt% NiO	3.5	1200	97.2	2.2	0.6	24
Si	0	1250	44.4	0	55.6	48
Si + polymer binder + polymer additive	3.5	1250	86.4	7.6	6	24
Si	0	1350	98.1	0	1.9	12
Si + polymer binder + polymer additive	3.5	1350	94.3	5.7	ND	3

TABLE IV.—SURFACE AREA AND
AVERAGE PARTICLE SIZE OF
FUMED SILICA, POLYMER CHAR,
AND CARBON BLACK

Material	Surface area, m^2/g	Average particle size, μm
Fumed silica	100±3	0.25
Polymer char	800±20	<0.1
Carbon black	560±15	<0.1
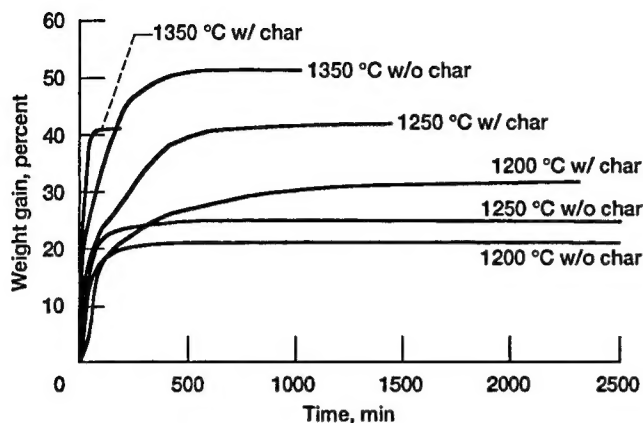
Figure 1.—Isothermal TGA curves showing the effect of temperature on nitridation kinetics of attrition milled silicon powder compacts with and without 3.5 wt % polymer char.
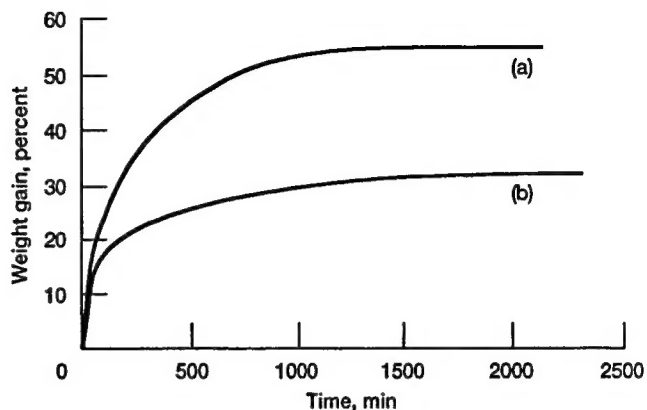
Figure 2.—Isothermal TGA curves for silicon nitrided at 1200 °C in 1 atm nitrogen (a) silicon + 3.5 wt % char (from binder) + 2.5 wt % NiO, (b) silicon + 3.5 wt % char (from binder and additive).
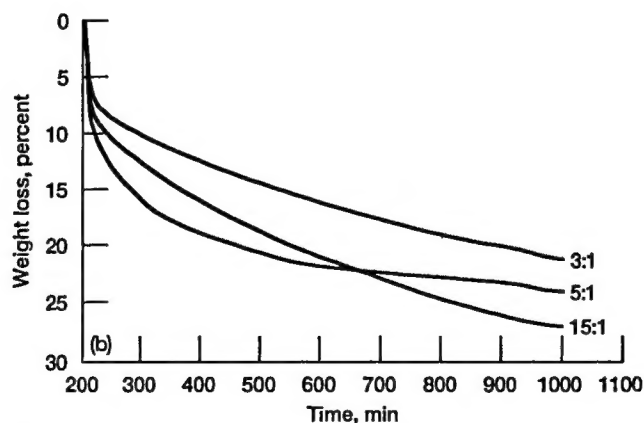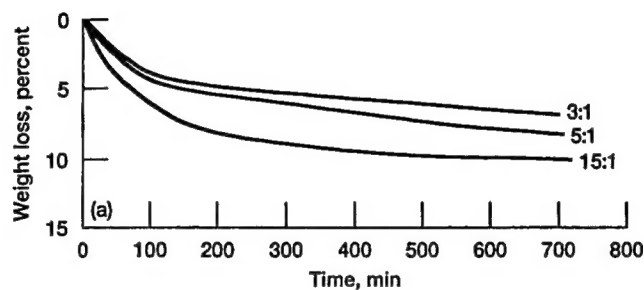

Figure 3.—TGA curves showing effects of temperature and carbon to silica molar ratio on nitridation kinetics of fumed silica and carbon black. (a) 1200 °C. (b) 1350 °C.
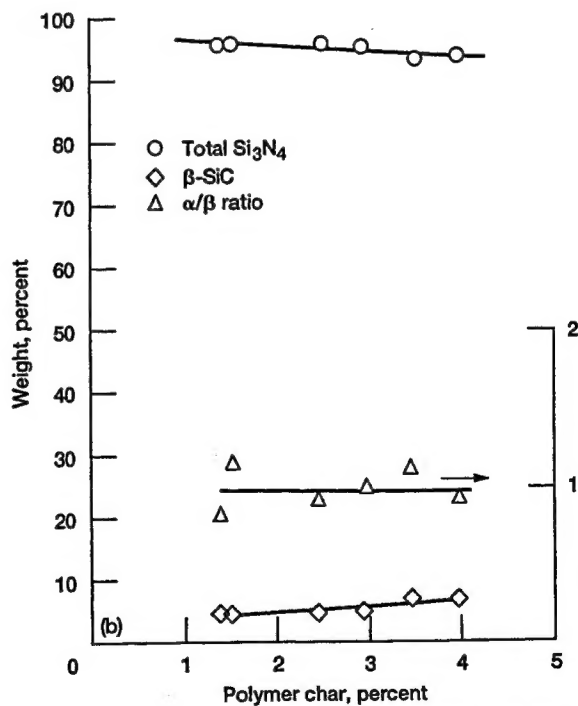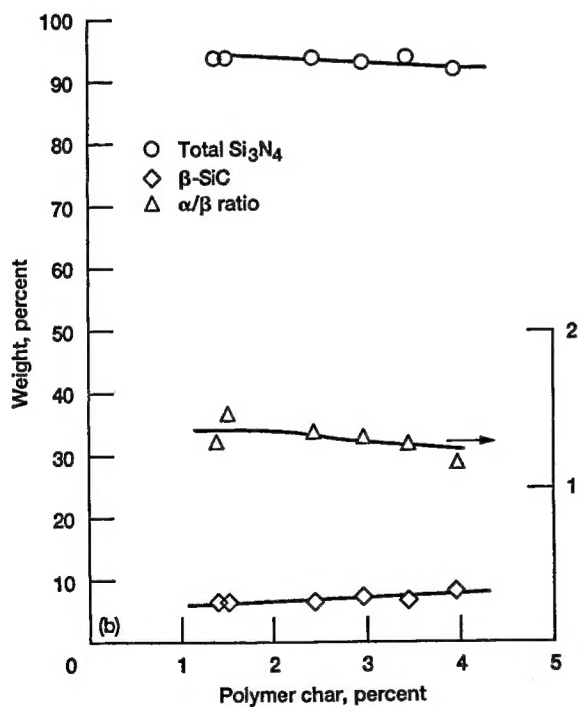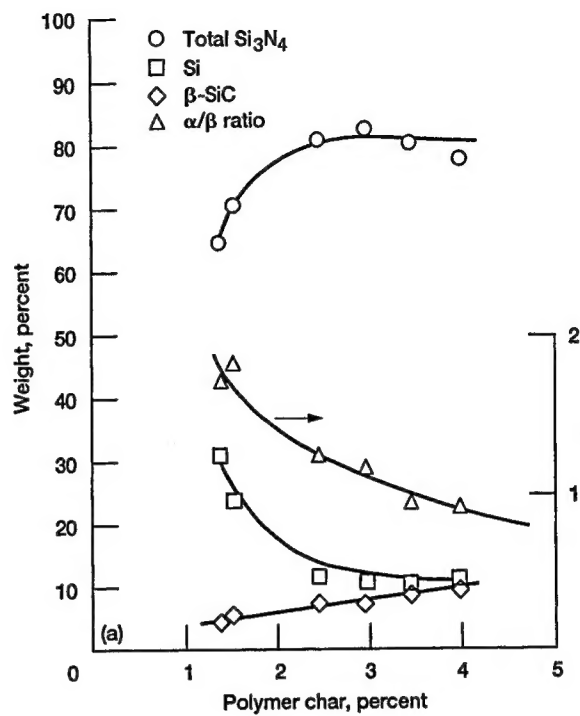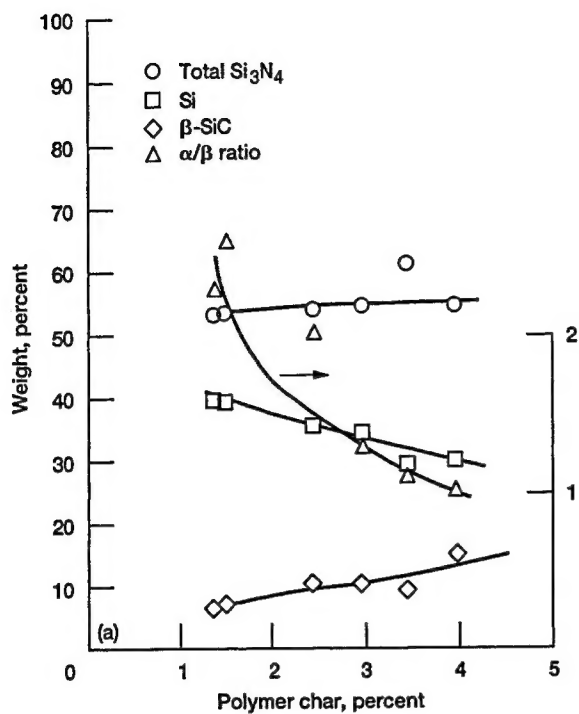
Figure 4.—Variation of phase composition of nitrided silicon with polymer char at 1200 °C for 24 hr in 1 atm nitrogen. (a) Silicon without NiO. (b) Silicon with 2.5 wt % NiO.

Figure 5.—Variation of phase composition of nitrided silicon with polymer char at 1350 °C for 1 hr in 1 atm nitrogen. (a) Silicon without NiO. (b) Silicon with 2.5 wt % NiO.

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13. ABSTRACT (Maximum 200 words)

Effects of polymer char on nitridation kinetics of attrition milled silicon powder have been investigated from 1200 to 1350 °C. Results indicate that at and above 1250 °C, the silicon compacts containing 3.5 wt% polymer char were fully converted to Si_3N_4 after 24 hr exposure in nitrogen. In contrast, the silicon compacts without polymer char could not be fully converted to Si_3N_4 at 1350 °C under similar exposure conditions. At 1250 and 1350 °C, the silicon compacts with polymer char showed faster nitridation kinetics than those without the polymer char. As the polymer char content is increased, the amount of SiC in the nitrided material is also increased. By adding small amounts (~2.5 wt%) of NiO, the silicon compacts containing polymer char can be completely nitrided at 1200 °C. The probable mechanism for the accelerated nitridation of silicon containing polymer char is discussed.

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